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PIGMENTS WITH THE STRUCTURE “INORGANIC NUCLEUS IN A FERROMAGNETIC SHELL”

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The possibilities of obtaining pigments with the structure “inorganic nucleus in a ferromagnetic shell” by depositing nickel and copper ferrites on the surfaces of optical-glass microgranules are studied. The porous characteristics, the physical–chemical properties, and the surface structure of the synthesized pigments are investigated.

In the last few years there has emerged a trend to obtain materials for different purposes by fixing nanoparticles on the surfaces of microgranules of metals, oxides, sulfides, carbon, and others [1]. Nanoparticles adsorbed on surfaces lose the capability to stick to one another, and they exhibit high reactive power when interacting with binders and chemical resistance to acid and alkali media as well as good heat resistance. Obtaining nanodispersed powdered materials by chemical deposition is promising [2]. Deposition of nanoparticles by this method on the surfaces of microgranules of production wastes, specifically, optical glasses, will make it possible not only to solve the important ecological problem of salvaging wastes but also to obtain pigments for producing magnetic materials for different purposes.

Our objective in the present work is to investigate the possibility of synthesizing magnetic pigments by chemical deposition of nanoparticles of nickel and copper ferrites on the surfaces of microgranules of optical-glass wastes (OGW).

OGW slurry consisting of a pasty water mixture of finely dispersed powders of optical glasses and polishing powder — electrocorundum, glycerin, solar emulsion, and surfactants — was used as the initial material. The slurry was dried at $100 \pm 5^\circ\text{C}$ to moisture content of 0.5%. The powder obtained was passed through a sieve with cell diameter $40\ \mu\text{m}$.

At the first stage the surface of the OGW microgranules was covered with a silica gel shell, having a high chemical

activity with respect to any of a large number of compounds with different functional groups [3]. The OGW particles were covered with silicon oxide using the procedure described in [4]. A weighed portion of OGW powder was suspended in boiling distilled water. A solution of liquid sodium glass (LSG) with the composition $\text{Na}_2\text{O} \cdot 2.45\text{SiO}_2$ (GOST 13079–81) with 2 mass% SiO_2 was added by drops to the suspension obtained. The ratio of the OGW powder to SiO_2 in the LSG solution was 7–8 (reservoir modulus). After all of the computed amount of LSG solution was introduced, the suspension was cooled to room temperature and the precipitate obtained was washed on a filter with distilled water. After the precipitate was dried at $100 \pm 5^\circ\text{C}$ it was heat treated at 500°C in a muffle furnace for 2 h.

A 0.2 M solution of iron (II), nickel, and copper chlorides (taken in the ratio of 12 : 1 : 1) was precipitated in a single stage by a solution of NaOH onto the surface of OGW microgranules with a silica gel shell [4]. The quantity of the precipitating agent was chosen so that after precipitation the pH of the mixture was in the range 12–13. Next, the suspension was rapidly oxidized by adding a solution of NaClO_3 . The precipitate obtained was washed with water and dried at 200°C , after which it was heat treated at 800°C for 1 h.

The formation of a bilayer coating on the surface of OGW microgranules was monitored by means of ξ -phorometry to determine the ξ potentials. The following parameters of the experimental 0.05% water solutions were measured on a Zetaphorometry IV (France) microelectrophorometer: viscosity, dielectric constant, and electrophoretic mo-

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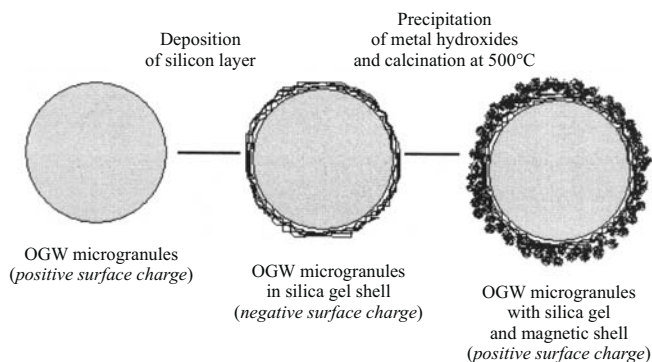


Fig. 1. Scheme illustrating the formation of the pigment "inorganic nucleus (OGW microgranules)/ferromagnetic shell."

bility of the particles. The magnitude of the ξ potential was calculated from the Smoluchowski equation:

$$\xi = \frac{4\pi\mu\eta}{\varepsilon},$$

where μ is the electrophoretic mobility of the particles, η is the viscosity, and ε is the dielectric constant.

Phase formation was monitored by x-ray phase analysis performed with a DRON-3 (CuK_α radiation) diffractometer. The thermographic investigations were performed on a Q-1000 DTA analyzer, manufactured by the MOM Company (Hungary), in the temperature interval 20–1000°C. The microstructure of the powders was determined by scanning electron microscopy using the LEO 1420 apparatus. A layer of gold was deposited on surfaces of the samples in a VUP-2K vacuum deposition apparatus.

Sorption of water vapor by the samples was conducted by holding the samples for 20 days (the period of time with the most intense absorption of moisture) in exsiccators with water vapor pressure 0.8, 9.8, and 17.2 mm Hg, set by the corresponding solutions of sulfuric acid [5] at room temperature. The water content in the sample was judged according to the mass difference between the initial sample, heated at 100°C, and the sample after being heated in an exsiccator.

The sorption volume of the pores in the samples was determined according to the sorption of benzene at 20°C in a vacuum adsorption apparatus with McBane–Baker spring quartz balances [6]. The initial pressure was 10^{-4} atm. The relative pressure was set to 0.9, after which the curve was extrapolated to 1.0. The BET method was used to determine the porous characteristics of the samples. The average radius of the pores was calculated according to the formula

$$r_{\text{av}} = \frac{2V_s}{S_{\text{sp}} \times 10^6},$$

where r_{av} is the average radius of the pores (in nm), V_s is the maximum sorption volume (in cm^3/g), and S_{sp} is the specific surface area (in m^2/g).

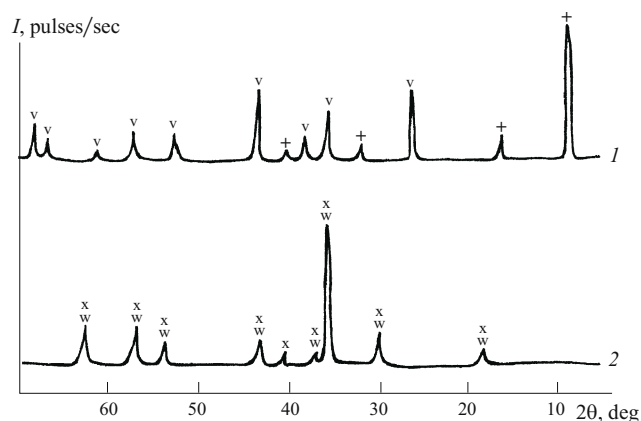


Fig. 2. X-ray diffraction pattern of the samples: 1) OGW; 2) pigment; v) $\alpha\text{-Al}_2\text{O}_3$; +) $\beta'\text{-NaAl}_7\text{O}_{11}$; w) NiFe_2O_4 ; x) CuFe_2O_4 .

The Curie temperature was determined according to the temperature dependence of the specific saturation magnetization.

It was found that after treatment, with a negatively charged colloidal solution of LSG (the ξ potential is -7.81 mV), of OGW microgranules charged positively beforehand (the ξ potential is -7.63 mV) their surface acquires a negative charge (the ξ potential is -5.28 mV). This suggests that silica gel SiO_2 coagulates directly on the surface of OGW particles. After precipitation of metal hydroxides on a negatively charged surface of a silica gel shell consisting of water solutions of the indicated salts, the particles of coagulant become positively charged (the ξ potential is 13.83 mV). Thus, recharging of the surfaces of the microgranules is observed at each stage of their treatment. Therefore, the coagulation of SiO_2 gel and precipitation of hydroxides occur directly on the surfaces of OGW particles. The overall scheme of the process resulting in pigment formation is displayed in Fig. 1.

According to XPA data, corundum $\alpha\text{-Al}_2\text{O}_3$ and sodium aluminate $\beta'\text{-NaAl}_7\text{O}_{11}$ (probably formed when optical glasses are polished using electrocorundum in an alkaline medium at high temperature developed as these surfaces are rubbed) are present in the initial OGW powder (Fig. 2, curve 1). The glass contained in OGW is x-ray amorphous.

Two endothermal effects — at 135 and 620°C — and an exothermal effect at 320°C are observed in the DTA trace of OGW powder (Fig. 3a). The first endothermal effect, associated with a change in the mass of the sample, corresponds to the release of water and the second corresponds to the melting of the sample. Complete decomposition of glycerin and surfactants occurs in the temperature range 260–410°C. The total mass loss at 410°C is 2%.

The DTA trace of OGW powder with a silica coating has one distinct endothermal effect at 660°C. This effect is not associated with a mass change and is due to melting of the sample (Fig. 3b). It should be noted that OGW powder with a silica layer deposited possesses high refractoriness — the

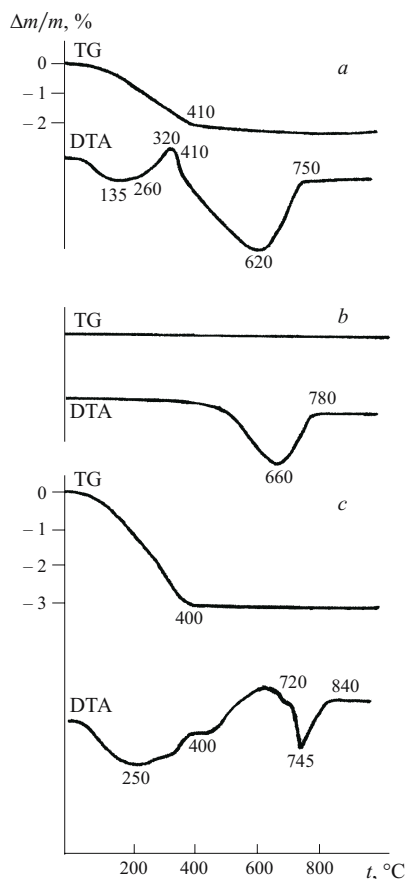


Fig. 3. Results of a complex thermal analysis of the samples: *a*) OGW; *b*) OGW with silica gel shell; *c*) pigment.

TABLE 1.

Sample	Water vapor pressure, mm Hg	Moisture content, %
OGW with silica	0.8	0.5
gel shell	9.8	1.3
	17.2	2.2
Pigment	0.8	28.0
	9.8	35.0
	17.2	47.0

melting temperature of a sample increases by 30°C. X-ray phase analysis of silica-coated powder did not reveal any new phases, since the silica formed is x-ray amorphous.

The DTA trace of the obtained powdered pigment, dried at 50°C, has two distinct endothermal effects — at 250 and 745°C. The first one is accompanied by a decrease in the mass of the sample and is associated with the removal of water; the second is due to melting of the sample (Fig. 3*c*). The data on the change in mass during heating show that on heating up to 400°C the sample loses 3% of its mass. X-ray phase analysis of the pigment shows the presence of spinels NiFe_2O_4 and CuFe_2O_4 (Fig. 2, curve 2).

In the photomicrographs the initial OGW powder consists of particles up to 20 μm in size with diverse shapes. Surface relief can be seen clearly on some of them (Fig. 4*a*). A silica coating formed on the surface of OGW microgranules hides their initial texture, but the initial shape of the particles remains (Fig. 4*b*). The surface of the pigment particles is completely coated with a crust of flaky crystals (Fig. 4*c*), which according to the XPA data are ferromagnetic nickel and copper spinels. It should be noted that the shape of the nickel and copper ferrite particles precipitated by the method indicated above in the absence of OGW microgranules is spherical — diamond-shaped and the average particle size is 200 – 300 nm (Fig. 4*d*).

Data on the sorption capacity of the samples obtained are presented in Table 1.

As one can see, the OGW microgranules in a silica gel shell essentially do not sorb moisture, which agrees with the data of [7]. The capacity of the pigment obtained to sorb water vapor is much higher — 47.0% at water vapor pressure 17 mm Hg.

Sorption isotherms of OGW samples with a silica coating and pigment are presented in Fig. 5. Analysis of the results shows that the benzene vapor adsorption isotherms of these samples differ substantially: the isotherms of an OGW sample with a silica shell in the experimental range of the relative pressure P/P_s has a very narrow hysteresis loop (the maximum sorp-

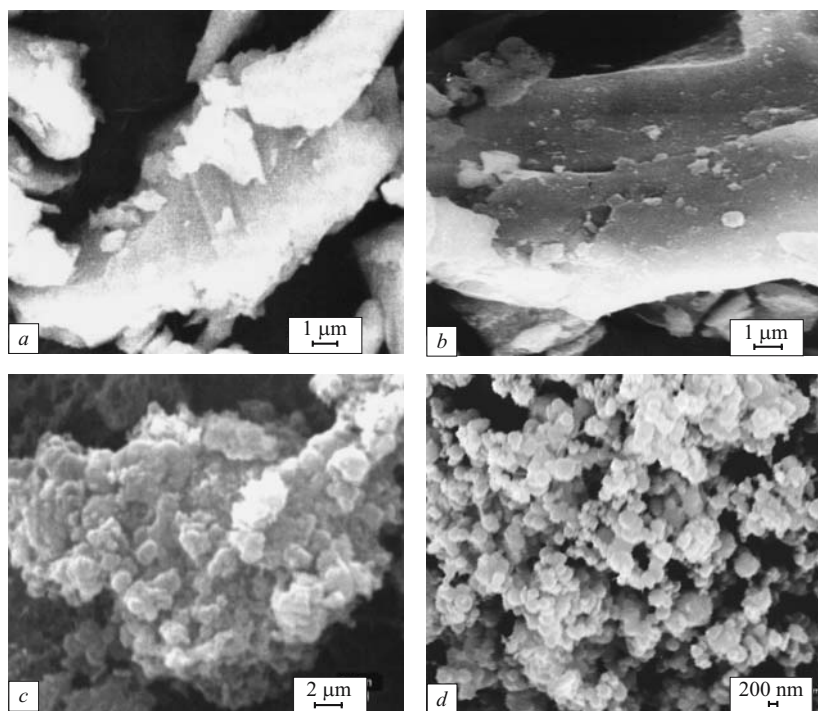


Fig. 4. Electron-microscopic photographs of samples: *a*) OGW; *b*) OGW with silica gel shell; *c*) pigment; *d*) nickel and copper ferrites (deposited without OGW) powder.

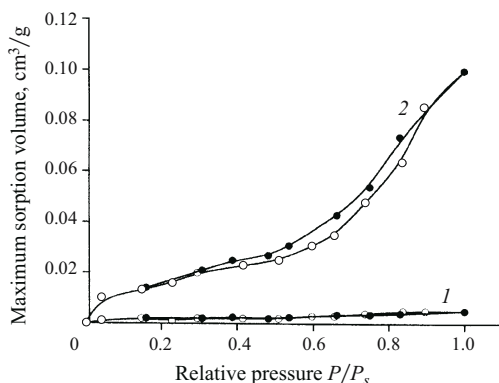


Fig. 5. Sorption isotherms for benzene vapor on OGW samples with a silica gel shell (1) and pigment (2).

tion volume of the sample is of the order of $0.005 \text{ cm}^3/\text{g}$. The isotherm of the pigment sample possesses a wider hysteresis loop, covering a quite large range of relative pressures (0.1 – 0.9).

The parameters of the samples are given in Table 2. Evidently, the pigment possesses a larger sorption volume and a substantial specific surface area.

The temperature dependence of the specific saturation magnetization for pigment is presented in Fig. 6. Its value at room temperature is $45.84 \text{ G} \cdot \text{cm}^3 \cdot \text{g}^{-1}$, and the Curie temperature is 446°C . When pigment is introduced in a magnetic field, a clear orientation of the pigment particles in the direction of the field can be seen. Therefore, the entire surface of the pigment particles is magnetic. Investigations have shown that the powder synthesized without OGW is characterized by the same magnetic properties.

Paint with viscosity 80 sec according to the VZ-4 viscosimeter was obtained on the basis of AS-528 polyacrylic lacquer and the synthesized pigment. The paint was deposited by pouring on plastic, wood, cardboard, and paper. Coating formation in a magnetic field makes it possible to obtain materials with prescribed magnetic properties [8]. The hardness of the coatings according to the M-3 pendulum apparatus is 0.1 arbitrary units.

In summary, pigments with the structure "inorganic nucleus in a ferromagnetic shell," characterized by highly extended porous surface area and good sorption properties as well as high reactivity when interacting with lacquer-paint binders have been obtained. The synthesized pigments are of interest as fillers for fabricating magnetic materials with prescribed properties.

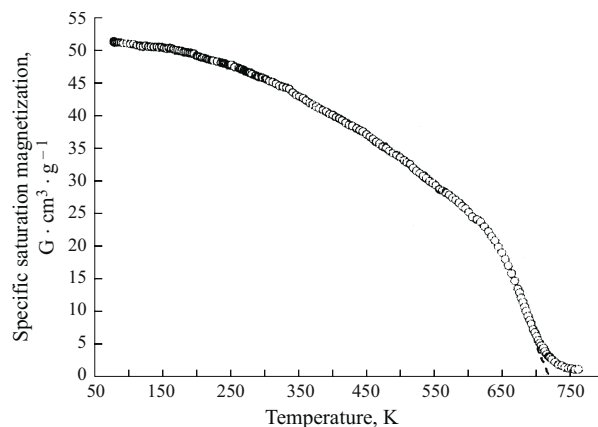


Fig. 6. Variation of the specific saturation magnetization of pigment as a function of temperature.

TABLE 2.

Sample	Maximum sorption volume, cm^3/g	Specific surface area, m^2/g	Average pore radius, nm
OGW with silica gel shell	0.005	3 – 4	–
Pigment	0.100	34	5.9

REFERENCES

1. S. P. Gubin, G. Yu. Yurkov, and N. A. Kataeva, "Microgranules and nanoparticles on their surface," *Neorg. Mater.*, **41**(10), 1159 – 1175 (2005).
2. I. V. Pishch and E. V. Radion, "Obtaining pigments by precipitation," *Steklo Keram.*, No. 4, 20 – 21 (1995).
3. *Modified Silica in Sorption, Catalysis, and Chromatography* [in Russian], Khimiya, Moscow (1986).
4. S. S. Airapetyan and A. G. Khachatryan, "Obtaining magnetic carriers, coated with a silica layer, on the basis of dispersed cobalt and zinc – nickel ferrites," *Zh. Neorg. Khim.*, **77**(1), 13 – 16 (2004).
5. *Concise Handbook of Chemistry* [in Russian], Naukova Dumka, Kiev (1974).
6. Zh. B. Galimov, G. G. Dubinina, and R. N. Masagurov, *Methods for Analyzing Catalysts for Petroleum Processing* [in Russian], Khimiya, Moscow (1973).
7. *Modified Silica in Sorption, Catalysis, and Chromatography* [in Russian], Khimiya, Moscow (1986).
8. Yu. I. Voronezhnev, V. V. Gol'dade, L. S. Pinchuk, and V. V. Snezhkov, *Electric and Magnetic Fields in the Technology of Polymer Composites* [in Russian], Nauka i Tekhnika, Minsk (1990).